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AN INTERPRETATION OF THE ETHYLENIC CARBIDIC AND
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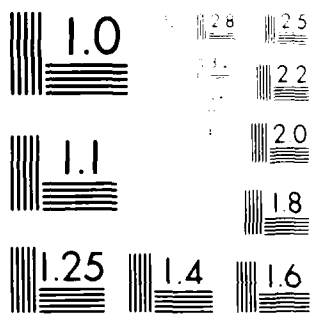
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An Interpretation Of The "Ethyleneic", "Carbideic", And
"Graphitic" Auger Lineshapes Of Chemisorbed Carbon Species

By
F. L. Hutson and D. E. Ramaker

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AN INTERPRETATION OF THE "ETHYLENIC", "CARBIDIC", AND "GRAPHITIC" AUGER LINESHAPES OF CHEMISORBED CARBON SPECIES

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Recently, Koef [1] reported the C KVV Auger lineshapes for C_2H_4 on $\text{Ni}(100)$ at a temperature of 100 K and for the decomposition products at 250, 300, and 600 K. We present detailed interpretations of these lineshapes, as well as for other previously reported carbidic and graphitic lineshapes [2].

The most significant results of this work can be summarized briefly as follows:

- 1) Although the lineshapes for the chemisorbed and comparable gas phase species are similar, they are composed of very different principal and satellite contributions; and 2) The Auger intensity arising from C-H bonds appear at much higher two-hole binding energy than that from C-M (metal) bonds. Thus the amount of C-H and C-M bond character in the surface species can be determined directly from the carbidic lineshapes. CH character is seen to remain even at 600 K on the $\text{Ni}(100)$ surface.

An interpretation of the theoretical gas phase ethylene Auger lineshape was reported previously [3]. It consists of the normal kvv component, and the resonantly excited (ke-vvv), initial-state shake (kv-vvv), and final-state shake (k-vvv) satellite components. Each component lineshape was determined as described previously [3]. The relative intensities of the components are determined by a least squares fit to the experimental lineshape, and are given in Table 1.

The components of the ethylenic (chemisorbed ethylene) lineshape are very different. This is because of transfer of an electron from the metal to the ethylene π^* orbital to screen the holes left by the Auger process. The ethylenic lineshape can be divided into the VV, $V\pi^*$, and $\pi^*\pi^*$ contributions, where V indicates collectively the normally occupied valence orbitals. The VV contribution should be directly related to that utilized for gas phase ethylene; however, the charge transfer decreases the effective number of holes, i.e., the transferred electron effectively cancels one hole. Therefore, we can model the principal kvv contribution in the ethylenic lineshape by utilizing the ke-vvv contribution from ethylene. Similarly the kv-vvv contribution in the ethylenic lineshape can be modeled by utilizing the kvv contribution from ethylene. The k-vvv contribution does not appear in the experimental ethylenic lineshape because it has been removed by the background subtraction and deconvolution processes [3]. The ke-v contribution from ethylene can be utilized to model the $V\pi^*$ contribution since it reflects the one-electron ethylene DOS. We must fold this with the π^* DOS. In the LCAO-MO approximation, the π^* orbital mixes with much of the Ni 3d valence band, indeed the hole left by the Auger decay involving the π^* orbital probability ends up on the Ni. Therefore we fold the ethylene DOS with the Ni 3d DOS as obtained from band calculations. Similarly, we model the $\pi^*\pi^*$ lineshape by utilizing the Ni L₂VV Auger lineshape. The relative intensity of these components, as given in Table 1, is determined by a fit to the experimental lineshape. Note the very different magnitudes of the various components, compared with the gas phase. If 1.3 electrons transferred from the Ni to the ethylene π^* orbital in the Auger final state, we should have $VV:V\pi^*:\pi^*\pi^* = 55:38:7$, in reasonable agreement with that in Table 1.

Previous Auger studies of the transition metal carbides indicate that correlation effects should be negligible in the Ni₂C lineshape [4]. Utilizing theoretical DOS [5], we find that the DOS self-fold, modulated with the appropriate atomic Auger matrix elements and allowing for core-hole screening, accounts for the experimental lineshape.

Comparison of the carbide lineshape with the carbidic lineshapes resulting from decomposition of C₂H₄/Ni(100), or hydrogenation of CO/Ni(100) or Ni(111) [2], reveal large differences. These differences suggest that the carbidic lineshapes result from hydrogenated C species (CH₃) on the surface. To confirm this, the lineshapes were fit to three components, which can be characterized as M₂M, M₂H, and H₂H, representing the respective folds of either the H-C or M-C DOS. The H-C DOS was taken to be that of methane gas [3]. The M-C DOS was that reported by Feibelman [5] for a metal carbide.

Excellent agreement with experiment is found; the results are summarized in Table I. For comparison, the expected component ratios for π -CH₂ and π -CH are given in Table 1. They indicate that at 600 K the dominant decomposition product of C₂H₄/Ni(100) is π -CH. For CO₂/Ni(100) or Ni(111), both π -CH and π -CH₂ are present, consistent with that suggested by XPS and EELS data [2].

Using similar techniques, the spectra obtained at 250 and 300 K in the decomposition of C₂H₄/Ni(100) [1] were interpreted. The results indicate that the 250 K spectra is consistent with di- σ bonded acetylene as suggested by EELS data [6]. The 300 K [1] spectra indicate a mixture consisting of about 65% di- σ bonded acetylene and 35% π -CH. A similar interpretation of the graphitic Auger spectra [2], obtained from the hydrogenation of CO/Ni(111) above 650 K, indicates that the graphite is weakly π bonded to the surface.

Table 1. Percent of each component for the Auger Lineshapes

Lineshape	k-vvv 15	k-vvvv 20	kvv 54	ke-vve 13	ke-v 2
Ethylene					
Ethylene:					
C ₂ H ₄ /Ni 100K	0	0	56	34	10
Carbide, Ni ₂ C					
Carbide:					
C ₂ H ₄ /Ni 600K	58	39	3		
CO ₂ /Ni(100)*	56	33	11		
CO ₂ /Ni(111)*	48	43	9		
Theory:					
π -CH	56	38	6		
π -CH ₂	44	44	11		

* Although the surface was heated to 600 K, the Auger data was taken after cooling back down to room temperature [2].

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*Supported in part by the Office of Naval Research

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